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A Generalized Time-Temperature-Transformation

Phase Diagram for Thermosetting Systems

by

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A GENERALIZED TIME-TEMPERATURE-TRANSFORMATION

PHASE DIAGRAM FOR THERMOSETTING SYSTEMS

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ABSTRACT

A generalized time-temperature-transformation diagram for
the thermosetting process is presented in which the four physical
states encountered (i.e., liquid, rubber, ungelled glass and
gelled glass) are related to the time and temperature of cure.
Gelation and vitrification, as a consequence of quenching morpho-
logical development and chemical conversion respectively, are
discussed with respect to control of material properties.

GELATION AND VITRIFICATION

Gelation and vitrification are two macroscopic phenomena which are encountered as a consequence of the reactions which convert a liquid to a solid in the thermosetting process. On the molecular level, gelation corresponds to the incipient formation of branched molecules of mathematically infinite molecular weight and occurs at a critical and calculable extent of reaction for the particular reactive system (1). A network develops by intramolecular reactions of branched molecules. Eventually the total mass can be one molecule. Macroscopically, gelation is associated with a dramatic increase in viscosity and a corresponding decrease in processibility. Gelation times are usually measured rheologically by the time between the beginning of the reaction and the attainment of a fixed viscosity.

Vitrification is the formation of a glassy solid. In thermosets this usually follows gelation and then occurs as a consequence of the network becoming tighter through further chemical reaction (crosslinking). A network structure will be a rubber (elastomer) at a given temperature if the segments between junction points of the network are flexible. If the segments are immobilized by further chemical reaction, or by cooling, the structure will change to a glassy (vitrified) state. Vitrification can retard further reaction. The overall transformation from liquid to gel to rubber to glass due to chemical reaction is termed "cure".

The properties of thermoset materials are intimately related to their formation (cure). The material properties therefore depend on the interplay between such factors as chemical reactants, viscosity prior to gelation, gelation, phase separation, vitrification, time-temperature paths of cure, and limits of thermal stability. The following section discusses a generalized time-temperature-transformation diagram (Figure 1) which is instructive for understanding these inter-relationships. It displays the four distinct material states which are encountered during cure; these are liquid, elastomer (rubber), ungelled glass and gelled glass.

The phase diagram may be constructed by measuring the time to gelation and the time to vitrification versus the isothermal temperature of cure (T_{cure}). A convenient technique involves using a torsion pendulum in which the specimen is an inert substrate (generally glass braid) impregnated with the system under investigation (2). Use of a supported sample permits investigation of the complete cure process versus time, and after cure the thermomechanical behavior with the same specimen. Times to gelation and to vitrification are measured by the lapsed time to the maxima of mechanical loss peaks: transition temperatures are similarly located with respect to temperature.

A GENERALIZED PHASE DIAGRAM FOR THERMOSETTING SYSTEMS (Figure 1)

Consideration of the cure of a liquid thermosetting system at a series of constant temperatures leads to the conclusion that there will be three types of behavior depending on the temperature of cure (3).

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At elevated isothermal temperatures, above the maximum glass transition temperature of the cured system ($T_{g\infty}$) but in the absence of degradation, a curing liquid gels and forms an elastomer (rubber) but does not vitrify.

At low temperatures, above the glass transition temperature of the reactants ($_{Resin}T_g$) but below a critical temperature ($_{gel}T_g$), the now viscous curing liquid can vitrify simply by an increase of molecular weight. If chemical reactions are quenched by vitrification it need not gel.

At intermediate temperatures ($_{gel}T_g < T_{cure} < T_{g\infty}$), the curing liquid first gels and later vitrifies. $_{gel}T_g$ is the isothermal temperature at which gelation and vitrification occur at the same time.

The time to gelation is expected to decrease exponentially with increasing temperature since the chemical conversion at gelation is constant according to Flory's gelation theory. Activation energies for the reactions leading to gelation can therefore be obtained from plots of the logarithm of the time to gelation versus reciprocal temperature in degrees Kelvin (3,4). The time to vitrify passes through a minimum between $_{gel}T_g$ and $T_{g\infty}$ (4). This reflects the competition between the increased rate constants for reaction and the increasing chemical conversion required for vitrification at higher temperatures.

It is apparent that if reactions are quenched by the process of vitrification ($T_{cure} < T_{g\infty}$), the glass transition temperature (T_g) of the system after isothermal cure will then equal the temperature of cure. The vitrification curve then provides the minimum time to reach the glass transition temperature which the reactive system can attain

at temperature T_{cure}. It also follows that $_{gel}T_g$ is the glass transition temperature of the reactive system at its point of gelation (3).

The cure/phase diagram therefore shows that the thermosetting process is usefully characterized by the three temperatures $_{Resin}T_g$, $_{gel}T_g$ and $T_{g\infty}$, which will vary from system to system.

The temperature between $_{gel}T_g$ and $T_{g\infty}$ at which the time to vitrify is a minimum may be of practical importance beyond being the most economical temperature for producing solid from fluid. As a consequence of the exothermic reactions, cure of specimens below this temperature will lead to the inside vitrifying before the outside; and vice versa. The volumetric shrinkage on vitrification will result in a skin-core structure for the latter case with built-in curing stresses. (This type of structure with residual thermal stresses also results on cooling after cure since the outside cools more rapidly than the inside.)

Whereas $_{Resin}T_g$, $_{gel}T_g$ and $T_{g\infty}$ are singular physical transition temperatures definable by a temperature (and time scale), thermal degradation cannot be so easily defined. Thermal degradation can lead to a gelled glass (as in Fig. 1); however other types of degradation can lead to other physical states (e.g. ungelled glass, liquid and gas).

The cure/phase diagram explains a number of practices in the field of thermosets.

If the storage temperature is below $_{gel}T_g$ a reactive fluid material will convert to a vitrified solid of low molecular weight which is stable and can be later liquified by heat and processed; above $_{gel}T_g$ the stored material will have a finite shelf-life for subsequent processing since gelation will occur before vitrification. (A gelled material does not flow in the usual sense.) This concept lies at the basis of a widespread technology which includes thermosetting molding compounds and "prepregs" with latent reactivity.

In general, if $T_{cure} < T_{g\infty}$, a reactive material will vitrify and full chemical conversion will be prevented; the material will then usually need to be

postcured above $T_{g\infty}$ for development of optimum properties. For the manufacture of objects of finite size it is necessary to go through a multi-step process because of the exothermic nature of the reactions. A more sophisticated approach for controlling highly exothermic systems is to cure the material by raising the temperature at a rate such that T_g and T_{cure} coincide.

For highly crosslinkable or rigid-chain polymeric materials $T_{g\infty}$ can be above the limits of thermal stability in which case the thermoset material may not have a measurable glass transition temperature and full chemical conversion of the original network-forming reactions would not be attained. For composite materials in which a component other than the cured resin is thermally sensitive, $T_{g\infty}$ for the thermosetting resin should be below temperatures which would lead to damage of any part of the assembly. (An example would be adhesive bonding of aluminum by a thermally stable epoxy.). Similarly, if a composite system cannot be heated above a limiting temperature because of its size, then the curing system should have its $T_{g\infty}$ below that limiting temperature. (An example would be painting an airplane in a hanger.)

It should be feasible to molecularly design systems such that T_g is above the temperature of cure. Suggestions include cure by small molecules which are able to diffuse through the glassy state, incorporation of sterically well situated reactive groups in the polymerizing system, and employment of systems with prominent glassy state relaxations (5).

The extent of cure affects not only the value of the glass transition but also properties at temperatures well below it. For example, it appears that the modulus at room temperature can be decreased and the intensity of the $T < T_g$ relaxations (as measured by the area under the loss peaks) can be increased by post-cure (6,7). This suggests that the free volume is increased and that the density at RT is decreased by the post-cure in spite of the increase of T_g.

This is presumably a result of the glassy state being further from equilibrium at RT the higher the T_g. Subsequent physical aging at room temperature leads to densification and embrittlement as the material spontaneously relaxes.

If $T_{g\infty}$ is below room temperature, the polymer system will be used as an elastomer.

The cure/phase diagram is being extended to two-phase systems. (Rubber is often incorporated in inherently brittle polymeric materials as a method for increasing toughness. The curing of rubber-modified systems often involves change from an initially homogeneous solution to a heterogeneous multiphase morphology.) Evidence has been presented to show that the process of gelation arrests the development of morphology, and therefore that the time to gelation can be used to control material properties (8). The gelation time can be varied by catalysts and temperature. Similarly, by reaction at different temperatures, a single chemical composition can produce distinctly different morphologies which in turn are responsible for distinctly different macroscopic behavior. The temperature of gelation, $T_{gelation}$, is therefore a characteristic one for defining the morphology developed isothermally by a particular system (9).

Rubber particles nucleate and grow during the polymerization process. In general, as in crystallization, nucleation is favored by low temperatures whereas growth is favored by high temperatures. The

overall extent of phase separation can therefore be expected to be at a maximum at intermediate temperatures (9).

Quenching of the development of morphological changes by the phenomenon of gelation may be explained by an abrupt decrease in diffusion of rubbery material to the growing domains of rubber which occurs in the transformation from a viscous liquid to a soft gel as infinite molecules form in the process of gelation. This is a longer range and larger scale diffusion process than that which is involved in the quenching of chemical reactions which occurs in the transformation from a rubbery state to a glassy state (vitrification) by restrictions on the more localized motions of chemically reactive parts of the molecules.

The cure/phase diagram is idealized in several respects.

If there are competing network-forming reactions having different reaction rates then different time-temperature paths will lead to different molecular networks in the fully cured materials and so to different material behavior. $T_{g\infty}$ and $_{gel}T_g$ will vary accordingly. For example, values for $T_{g\infty}$ may be higher after prolonged initial reaction at low rather than at high temperatures prior to completion of the reactions by post-cure (7).

Vitrification times will be longer than those measured operationally from the time to the peak of the mechanical loss maximum assigned to the vitrification process since vitrification, with respect to the quenching of reactions, is better defined when the rigidity levels off (6).

The macroscopic assignment of gelation by a rheological measurement (which corresponds to an isoviscosity measurement) does not necessarily correspond to its molecular definition (which corresponds to an isocompositional state). However, values obtained rheologically for the activation energies of reactions leading to gelation can be close to those determined from times to reach constant chemical conversion (6,10,11).

The phase-diagram (above) has been obtained experimentally from a series of isothermal reactions. A similar diagram can be obtained for a given system from a series of temperature-programmed scans from low to high temperature at different heating rates (7). A typical scan will then reveal glassy-state relaxations of the unreacted resin below its glass transition, $_{Resin}T_g$, gelation, vitrification, devitrification (i.e. T_g), and above $T_{g\infty}$ re-vitrification due to degradation.

CONCLUSION

Experimental examination of the phenomena encountered in the thermosetting process has led to a generalized time-temperature-transformation phase diagram which provides a theoretical and convenient basis for understanding the factors which bear on the molecular engineering of thermosetting materials.

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FIGURE CAPTION

Figure 1. Time-temperature-transformation diagram: time to gel and time to vitrify vs isothermal cure temperature. Resin T_g, gel T_g and $T_{g\infty}$ are critical temperatures in the phase diagram which shows the four states of materials encountered in the thermosetting process, i.e., liquid, rubber, ungelled glass, and gelled glass.

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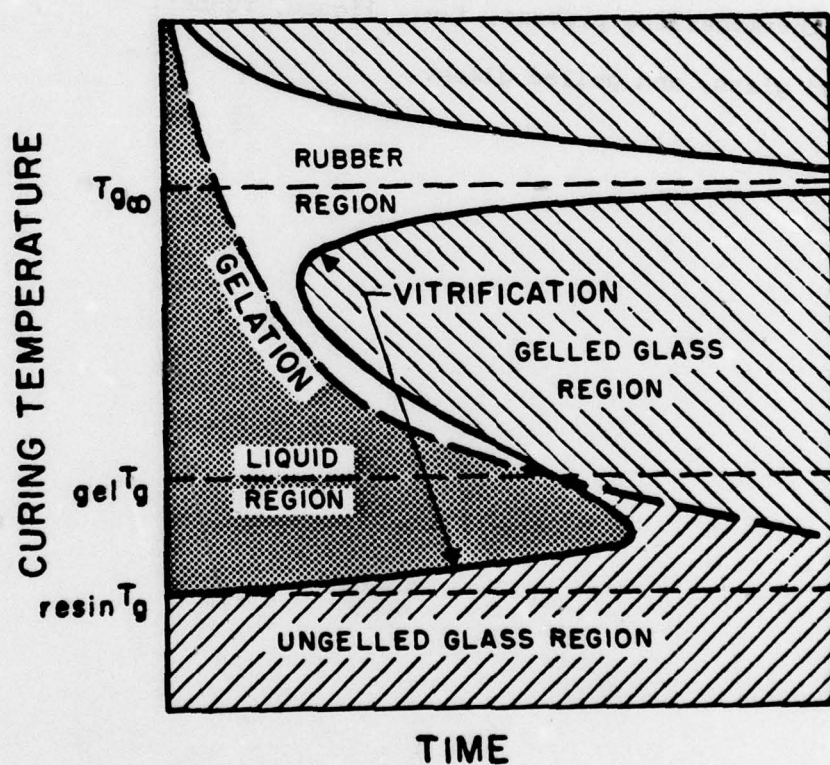## TIME-TEMPERATURE-TRANSFORMATION
PHASE DIAGRAM

Fig. 1

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